



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A01N 51/00, 47/40 // (A01N 51/00, 43:88, 43:56, 43:40, 43:30)		(11) International Publication Number: WO 97/40692
(21) International Application Number: PCT/EP97/01926		(43) International Publication Date: 6 November 1997 (05.11.97)
(22) International Filing Date: 17 April 1997 (17.04.97)		
(30) Priority Data: 1082/96	29 April 1996 (29.04.96)	CH
(71) Applicant for all designated States except US: NOVARTIS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).		
(72) Inventors; and (75) Inventors/Applicants for US only: SENN, Robert [CH/CH]; Riehenring 7, CH-4058 Basel (CH). MAIENFISCH, Peter [CH/CH]; Agentenstrasse 21, CH-4118 Rodersdorf (CH). WYSS, Peter [CH/CH]; Do Tia 14, CH-2748 Soubos (CH).		
(74) Agent: ROTH, Bernhard, M.; Novartis AG, Patent- und Markenabteilung, Klybeckstrasse 141, CH-4002 Basel (CH).		
(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).		

Published

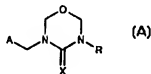
With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PESTICIDAL COMPOSITIONS

(57) Abstract

Composition for controlling insects and representatives of the order Acarina, which comprises a combination of variable amounts of one or more compounds of formula (A), in which A is an unsubstituted or, depending on the possibility of substitution on the ring system, mono- to tetrasubstituted, aromatic or non-aromatic monocyclic or bicyclic heterocyclic radical, in which the substituents of A can be chosen from the group consisting of C₁-C₃alkyl, C₁-C₃alkoxy, halogen, halo-C₁-C₃alkyl, cyclopropyl, halocyclopropyl, C₂-C₃alkenyl, C₂-C₃alkynyl, halo-C₂-C₃alkenyl, halo-C₂-C₃alkynyl, halo-C₁-C₃alkoxy, C₁-C₃alkylthio, halo-C₁-C₃alkylthio, allyloxy, propargyloxy, allylthio, propargylthio, haloallyloxy, haloallylthio, cyano and nitro; R is hydrogen, C₁-C₆alkyl, phenyl-C₁-C₃alkyl, C₃-C₆cycloalkyl, C₂-C₆alkenyl or C₂-C₆alkynyl; and X is N-NO₂ or N-CN, in the free form or in the salt form, if appropriate tautomers, in the free form or salt form, and one or more of the compounds (I) to CLXXXIV) mentioned according to the invention and at least one auxiliary. A method of controlling pests, a process for the preparation of the composition, its use and plant propagation material treated with it, and the use of the compound of formula (A) for the preparation of the composition, are described.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

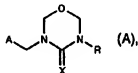
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KZ	Kazakhstan	PT	Portugal		
CN	China	LC	Saint Lucia	RO	Romania		
CU	Cuba	LI	Liechtenstein	RU	Russian Federation		
CZ	Czech Republic	LK	Sri Lanka	SD	Sudan		
DE	Germany	LR	Liberia	SE	Sweden		
DK	Denmark			SG	Singapore		
EE	Estonia						

PESTICIDAL COMPOSITIONS

The present invention relates to a composition which comprises a pesticidal active compound combination, a method for controlling pests with this composition, a process for the preparation of the composition, its use and plant propagation material treated with it, and the use of a compound of the following formula (A) for the preparation of the composition.

Certain mixtures of active compounds are proposed for pest control in the literature. However, the biological properties of these mixtures of known compounds are not completely satisfactory in the field of pest control, and for this reason there is a need to provide further mixtures having synergistic pest control properties, in particular for control of insects and representatives of the order Acarina. This object is achieved according to the invention by providing the present composition.

The invention accordingly relates to a composition for controlling insects and representatives of the order Acarina, which comprises a combination of variable amounts of one or more compounds of the formula



In which

A is an unsubstituted or, depending on the possibility of substitution on the ring system, mono- to tetrasubstituted, aromatic or non-aromatic monocyclic or bicyclic heterocyclic radical, in which the substituents of A are chosen from the group consisting of C₁-C₃alkyl, C₁-C₃alkoxy, halogen, halo-C₁-C₃alkyl, cyclopropyl, halocyclopropyl, C₂-C₃alkenyl, C₂-C₃alkynyl, halo-C₂-C₃alkenyl, halo-C₂-C₃alkynyl, halo-C₁-C₃alkoxy, C₁-C₃alkylthio, halo-C₁-C₃alkylthio, allyloxy, propargyloxy, allylthio, propargylthio, haloallyloxy, haloallylthio, cyano and nitro;

R is hydrogen, C₁-C₆alkyl, phenyl-C₁-C₄alkyl, C₃-C₆cycloalkyl, C₂-C₆alkenyl or C₂-C₆alkynyl; and

X is N-NO₂ or N-CN,

in the free form or in salt form, If appropriate tautomers, in the free form or salt form, and one or more of the compounds:

(I) aldicarb;	(XVIII) ethiofencarb;	(XXXV) teflubenzuron;
(II) azinphos-methyl;	(XIX) fenitrothion;	(XXXVI) terbufos;
(III) benfuracarb;	(XX) fenobucarb;	(XXXVII) triazamate;
(IV) bifenthrin;	(XXI) fenvalerate;	(XXXVIII) abamectin;
(V) buprofezin;	(XXII) formothion;	(XXXIX) fenobucarb;
(VI) carbofuran;	(XXIII) methiocarb;	(XL) tebufenozide;
(VII) dibutylaminothio;	(XXIV) heptenophos;	(XLI) fipronil;
(VIII) cartap;	(XXV) imidacloprid;	(XLII) beta-cyfluthrin;
(IX) chlorofluazuron;	(XXVI) isoprocarb;	(XLIII) sflafluofen;
(X) chloropyrifos;	(XXVII) methamidophos;	(XLIV) fenpyroximate;
(XI) cyfluthrin;	(XXVIII) methomyl;	(XLV) pyridaben;
(XII) lambda-cy-halothrin;	(XXIX) mevinphos;	(XLVI) fenazaquin;
(XIII) alpha-cypermethrin;	(XXX) parathion;	(XLVII) pyriproxyfen;
(XIV) zeta-Cypermethrin;	(XXXI) parathion-methyl;	(XLVIII) pyrimidifen;
(XV) deltamethrin;	(XXXII) phosalone;	(XLIX) nitenpyram;
(XVI) diflubenzuron;	(XXXIII) pirimicarb;	(L) NI-25, acetamiprid;
(XVII) endosulfan;	(XXXIV) propoxur;	
(LI) avermectin B ₁ (abamectin);		
(LII) a plant extract which is active against insects;		
(LIII) a preparation which comprises nematodes which are active against insects;		
(LIV) a preparation obtainable from <i>Bacillus subtilis</i> ;		
(LV) a preparation which comprises fungi which are active against insects;		
(LVI) a preparation which comprises viruses which are active against insects;		
(LVII) AC 303 630;	(LXVII) bendiocarb;	(LXXVII) carbaryl;
(LVIII) acephate;	(LXVIII) bensultap;	(LXXVIII) carbopheno-
(LIX) acrinathrin;	(LXIX) betacyfluthrin;	thion;
(LX) alanycarb;	(LXX) BPMC;	(LXXIX) chloethocarb;
(LXI) alphamethrin;	(LXXI) brofenprox;	(LXXX) chloroethoxyfos;
(LXII) amitraz;	(LXXII) bromophos A;	(LXXXI) chloromephos;
(LXIII) AZ 60541;	(LXXIII) butencarb;	(LXXXII) cis-res-methrin;
(LXIV) azinphos A;	(LXXIV) butocarbioxin;	(LXXXIII) clocthrin;
(LXV) azinphos M;	(LXXV) butylpyridaben;	(LXXXIV) clofentezin;
(LXVI) azocyclotin;	(LXXVI) cadusafos;	(LXXXV) cyanophos;

(LXXXVI) cycloprothrin;	(CXIX) hexaflumuron;	(CL) pyrachlophos;
(LXXXVII) cyhexatin;	(CXX) hexythiazox;	(CLI) pyrada-phenthion;
(LXXXVIII) demeton M;	(CXXI) iprobenfos;	(CLII) pyresmethrin;
(LXXXIX) demeton S;	(CXXII) isofenphos;	(CLIII) pyrethrum;
(XC) demeton-S-methyl;	(CXXIII) isoxathion;	(CLIV) RH 5992;
(XCI) dichlofenthion;	(CXXIV) ivermectin;	(CLV) salithion;
(XCII) dicliphos;	(CXXV) lambda- cyhalothrin;	(CLVI) sebufos;
(XCIII) diethion;	(CXXVI) malathion;	(CLVII) sulfotep;
(XCIV) dimethoate;	(CXXVII) mecarbam;	(CLVIII) sulprofos;
(XCV) diméthylvinphos;	(CXXVIII) mesulfenphos;	(CLIX) tebufenpyrad;
(XCVI) dloxathion;	(CXXIX) metaldehyde;	(CLX) tebuipirimphos;
(XCVII) edifenphos;	(CXXX) metolcarb;	(CLXI) telfuthrin;
(XCVIII) emamectin;	(CXXXI) milbemectin;	(CLXII) temephos;
(XCIX) esfenvalerate;	(CXXXII) moxidectin;	(CLXIII) terbam;
(C) ethion;	(CXXXIII) naled;	(CLXIV) tetrachloro- vinphos;
(CI) ethofenprox;	(CXXXIV) NC 184;	(CLXV) thiafenox;
(CII) ethoprophos;	(CXXXV) omethoate;	(CLXVI) thiodicarb;
(CIII) etrimphos;	(CXXXVI) oxamyf;	(CLXVII) thiofanox;
(CIV) fenamiphos;	(CXXXVII) oxydeme- thon M;	(CLXVIII) thionazin;
(CV) fenbutatin oxide;	(CXXXVIII) oxydeprofos;	(CLXIX) thuringiensin;
(CVI) fenothiocarb;	(CXXXIX) permethrin;	(CLXX) tralomethrin;
(CVII) fenpropathrin;	(CXL) phenhoate;	(CLXXI) triarthen;
(CVIII) fenpyrad;	(CXLII) phosmet;	(CLXXII) triazophos;
(CIX) fenthion;	(CXLIII) phoxim;	(CLXXIII) triazuron;
(CX) fluazinam;	(CXLIV) pirimiphos M;	(CLXXIV) trichlorofon;
(CXI) flucycloxuron;	(CXLV) pirimiphos A;	(CLXXV) triflumuron;
(CXII) flucythrinate;	(CXLVI) promecarb;	(CLXXVI) trimethacarb;
(CXIII) flufenoxuron;	(CXLVII) propaphos;	(CLXXVII) vamidothion;
(CXIV) flufenprox;	(CXLVIII) prothiofos;	(CLXXVIII) xylylcarb;
(CXV) fonophos;	(CXLIX) prothoate;	(CLXXIX) YI 5301/5302;
(CXVI) fosthiazate;		(CLXXX) zetamethrin;
(CXVII) fubfenprox;		(CLXXXI) DPX-MP062;
(CXVIII) HCH;		

(CLXXXII) RH-2485; (CLXXXIII) D 2341; or (CLXXXIV) XMC (3,5-xylyl-methylcarbamate),

and at least one auxiliary.

Compounds of the formula (A) are described in EP-A-580553.

The compounds (I) to (CLXXXIV) are known to the expert. In particular

- (I) 2-methyl-2-(methylthio)propionaldehyde O-methylcarbamoyloxime (aldicarb) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 16;
- (II) S-3,4-dihydro-4-oxo-1,2,3-benzotriazin-3-ylmethyl O,O-dimethyl phosphorodithioate (azinphos-methyl) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 46;
- (III) ethyl N-[2,3-dihydro-2,2-dimethylbenzofuran-7-yloxycarbonyl(methyl)aminothio]-N-isopropyl- β -alaninate (benfuracarb) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 57;
- (IV) 2-methylbiphenyl-3-ylmethyl (Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate (bifenthrin) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 73;
- (V) 2-tert-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazan-4-one (buprofezin) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 105;
- (VI) 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate (carbofuran) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 126;
- (VII) 2,3-dihydro-2,2-dimethylbenzofuran-7-yl (dibutylaminothio)-methylcarbamate (carbosulfan) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 129;
- (VIII) S,S'-(2-dimethylaminotrimethylene) bis(thiocarbamate) (cartap) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 132;
- (IX) 1-[3,5-dichloro-4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenyl]-3-(2,6-difluorobenzoyl)-urea (chlorofluazuron) is known from The Pesticide Manual, 9th Ed. (1991), The British Crop Protection Council, London, page 143;

- (X) O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate (chlorpyrifos) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 166;
- (XI) (RS)- α -cyano-4-fluoro-3-phenoxybenzyl (1RS)-cis-trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (cyfluthrin) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 198;
- (XII) Mixture of (S)- α -cyano-3-phenoxybenzyl Z-(1R)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate and (R)- α -cyano-3-phenoxybenzyl Z-(1S)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate (lambda-cyhalothrin) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 203;
- (XIII) Racemate of (S)- α -cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (R)- α -cyano-3-phenoxybenzyl (1S)-cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (alpha-cypermethrin) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 210;
- (XIV) A mixture of (S)- α -cyano-3-phenoxybenzyl (1RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (S)- α -cyano-3-phenoxybenzyl (3RS)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (zeta-cypermethrin) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, page 265;
- (XV) (S)- α -cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate (deltamethrin) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 232;
- (XVI) (4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea (diflubenzuron) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 281;
- (XVII) (1,4,5,6,7,7-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenebismethylene) sulfite (endosulfan) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 332;
- (XVIII) α -ethylthio-o-tolyl methylcarbamate (ethiofencarb) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 343;

- (XIX) O,O-dimethyl O-4-nitro-m-tolyl phosphorothioate (fenitrothion) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 369;
- (XX) 2-sec-butylphenyl methylcarbamate (fenobucarb) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 371;
- (XXI) (RS)- α -cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate (fenvalerate) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 388;
- (XXII) [formyl(methyl)carbamoylmethyl] O,O-dimethyl phosphorodithioate (formothion) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 440;
- (XXIII) 4-methylthio-3,5-xylyl methylcarbamate (methiocarb) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, page 677;
- (XXIV) 7-chlorobicyclo[3.2.0]hepta-2,6-dien-6-yl dimethylphosphate (heptenophos) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, page 467;
- (XXV) (6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidenamine (imidacloprid) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 491;
- (XXVI) 2-isopropylphenyl methylcarbamate (isoprocab) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 504;
- (XXVII) O,S-dimethyl phosphoramidothioate (methamidophos) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 563;
- (XXVIII) S-methyl N-(methylcarbamoyloxy)thioacetimidate (methomyl) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 570;
- (XXIX) methyl 3-(dimethoxyphosphinoyloxy)but-2-enoate (mevinphos) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 592;
- (XXX) O,O-diethyl O-4-nitrophenyl phosphorothioate (parathion) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 648;
- (XXXI) O,O-dimethyl O-4-nitrophenyl phosphorothioate (parathion-methyl) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 650;

- (XXXII) S-6-chloro-2,3-dihydro-2-oxo-1,3-benzoxazol-3-ylmethyl O,O-diethyl phosphordithioate (phosalone) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 674;
- (XXXIII) 2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (pirimicarb) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 690;
- (XXXIV) 2-isopropoxyphenyl methylcarbamate (propoxur) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 727;
- (XXXV) 1-(3,5-dichloro-2,4-difluorophenyl)-3-(2,6-difluorobenzoyl)urea (teflubenzuron) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 790;
- (XXXVI) S-tert-butylthiomethyl O,O-dimethyl phosphorodithioate (terbufos) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 795;
- (XXXVII) ethyl (3-tert-butyl-1-dimethylcarbamoyl-1H-1,2,4-triazol-5-yl-thio)acetate (triazamate) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 1006;
- (XXXVIII) abamectin is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 3;
- (XXXIX) 2-sec-butylphenyl methylcarbamate (fenobucarb) is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 371;
- (XL) N-tert-butyl-N'-(4-ethylbenzoyl)-3,5-dimethylbenzohydrazide (tebufenozide) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 943;
- (XLI) (±)-5-amino-1-(2,6-dichloro- α,α,α -trifluoro-p-tolyl)-4-trifluoromethyl-sulfinylpyrazole-3-carbonitril (fipronil) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 463;
- (XLII) α -cyano-4-fluoro-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate (beta-cyfluthrin) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 250;
- (XLIII) (4-ethoxyphenyl)[3-(4-fluoro-3-phenoxyphenyl)propyl](dimethyl)silane (silafiufoen) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 912;

- (XLIV) tert-butyl (E)- α -(1,3-dimethyl-5-phenoxy-pyrazol-4-yl-methylenamino-oxy)-p-toluate (fenpyroximate) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 450;
- (XLV) 2-tert-butyl-5-(4-tert-butylbenzylthio)-4-chloropyridazin-3(2H)-one (pyridaben) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 879;
- (XLVI) 4-tert-butylphenethyl quinaldin-4-yl ether (fenazaquin) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 426;
- (XLVII) 4-phenoxyphenyl (RS)-2-(pyridyloxy)propyl ether (pyriproxyfen) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 887;
- (XLVIII) 5-chloro-N-[2-[4-(2-ethoxyethyl)-2,3-dimethylphenoxy]ethyl]-6-ethylpyrimidin-4-amine (pyrimidifen) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 887;
- (XLIX) (E)-N-(6-chloro-3-pyridylmethyl)-N-ethyl-N'-methyl-2-nitrovinylidenediamine (nitenpyram) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 736;
- (L) (E)-N¹-[(6-chloro-3-pyridyl)methyl]-N²-cyano-N¹-methylacetamidine (NI-25, acetamiprid) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 730;
- (LI) avermectin B₁ (abamectin) is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 1;
- (LII) a plant extract which is active against insects, in particular (2R,6aS,12aS)-1,2,6,6a,12,12a-hexahydro-2-isopropenyl-8,9-dimethoxy-chromeno[3,4-b]furo[2,3-h]-chromen-6-one (rotenone), is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 758; and an extract from Azadirachta indica, in particular azadirachtin, is known from The Pesticide Manual, 10thEd. (1991), The British Crop Protection Council, London, Page 54; and
- (LIII) a preparation which comprises nematodes which are active against insects, preferably Heterorhabditis bacteriophora, Heterorhabditis megidis is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 560; one comprising Steinernema feltiae is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 920, and one comprising Steinernema

- 9 -

- scapterisci is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 921;
- (LV) a preparation obtainable from *Bacillus subtilis* is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 62; or one obtainable from a *Bacillus thuringiensis* strain, with the exception of compounds isolated from GC91 or from NCTC11821, is known;
- (LV) a preparation which comprises fungi which are active against insects, preferably *Verticillium lecanii*, is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 1040; one comprising *Beauveria brogniartii* is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 69; and one comprising *Beauveria bassiana* is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 69;
- (LVI) a preparation which comprises viruses which are active against insects, preferably Neodiprion sertifer NPV, is known from The Pesticide Manual, 9thEd. (1991), The British Crop Protection Council, London, Page 616; one comprising *Mamestra brassicae* NPV is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 633; and one comprising *Cydia pomonella* granulosus virus is known from The Pesticide Manual, 10thEd. (1994), The British Crop Protection Council, London, Page 247;
- (CLXXXI) Indeno[1,2-e] [1,3,4] oxadiazine-4a (3H)-carboxylic acid, 7-chloro-2,5-dihydro-2-[[[(methoxycarbonyl)[(4-trifluoromethoxy)phenyl]amino]carbonyl]-, methyl ester (DPX-MP062), is known from the Brighton Crop Protection Conference, 1996, 449- 456;
- (CLXXXII) N'-tert-butyl-N'-(3,5-dimethylbenzoyl)-3-methoxy-2-methylbenzohydrazide (RH-2485, methoxyfenozide) is known from the Brighton Crop Protection Conference, 1996, 481- 486; and
- (CLXXXIII) N'-[4-methoxybiphenyl-3-yl]hydrazinecarboxylic acid isopropyl ester (D 2341) is known from the Brighton Crop Protection Conference, 1996, 487- 493.

The compounds of the formula (A) can in some cases be in the form of tautomers. For example, if R is hydrogen, corresponding compounds of the formula (A), i.e. those having a 3-H-4-imino-perhydro-1,3,5-oxadiazine partial structure, can be in equilibrium with the particular tautomers which contain a 4-amino-1,2,5,6-tetrahydro-1,3,5-oxadiazine partial structure. Compounds of the formula (A) above and below are accordingly also to be un-

derstood as meaning, where appropriate, corresponding tautomers, even if the latter are not mentioned specifically in each case.

Compounds of the formula (A) which contain at least one basic centre can form, for example, acid addition salts. These are formed, for example, with strong inorganic acids such as mineral acids, for example perchloric acid, sulfuric acid, nitric acid, nitrous acid, a phosphoric acid or a hydrogen halide acid, with strong organic carboxylic acids, such as C₁-C₄alkanecarboxylic acids which are unsubstituted or substituted, for example by halogen, for example acetic acid, such as dicarboxylic acids which are saturated or unsaturated, for example oxalic, malonic, succinic, maleic, fumaric or phthalic acid, such as hydroxycarboxylic acids, for example ascorbic, lactic, malic, tartaric or citric acid, or such as benzoic acid, or with organic sulfonic acids, such as C₁-C₄alkane- or arylsulfonic acids which are unsubstituted or substituted, for example by halogen, for example methane- or p-toluenesulfonic acid. Compounds of the formula (A) with at least one acid group can furthermore form salts with bases. Suitable salts with bases are, for example, metal salts, such as alkali metal or alkaline earth metal salts, for example sodium, potassium or magnesium salts, or salts with ammonia or an organic amine, such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower alkylamine, for example ethyl-, diethyl-, triethyl- or dimethyl-propyl-amine, or a mono- di- or trihydroxy-lower alkylamine, for example mono-, di- or triethanolamine. If appropriate, corresponding inner salts can furthermore be formed. Agrochemically advantageous salts are preferred in the context of the invention. As a result of the close relationship between the compounds of the formula (A) in the free form and in the form of their salts, the free compounds of the formula (A) and their salts above and below are also appropriately and expediently to be understood as meaning, where appropriate, the corresponding salts and the free compounds of the formula (A). The same applies correspondingly to tautomers of compounds of the formula (A) and salts thereof. In each case the free form is in general preferred.

Compositions which comprise the compound of the formula (A) in the free form are preferred in the context of the present invention.

The general terms used above and below have the meanings given below, unless defined otherwise.

Heteroatoms in the cyclic base skeleton of the heterocyclic radical R are all elements of the Periodic Table which can form at least two covalent bonds. N and S are preferred.

Halogen - as a group per se and as a structural element of other groups and compounds, such as of haloalkyl, haloalkylthio, haloalkoxy, halocyclopropyl, haloalkenyl, haloalkynyl, haloallyloxy and haloallylthio - is fluorine, chlorine, bromine or iodine, in particular fluorine, chlorine or bromine, especially fluorine or chlorine, in particular chlorine..

Unless defined otherwise, carbon-containing groups and compounds in each case contain 1 up to and including 6, preferably 1 up to and including 3, in particular 1 or 2, carbon atoms.

Cycloalkyl is cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, preferably cyclopropyl.

Alkyl - as a group per se and as a structural element of other groups and compounds, such as of phenylalkyl, haloalkyl, alkoxy, haloalkoxy, alkylthio and haloalkylthio - is, in each case taking into due consideration the number of carbon atoms, defined from case to case, contained in the corresponding group or compound, either straight-chain, i.e. methyl, ethyl, propyl, butyl, pentyl or hexyl, or branched, for example, isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl, neopentyl or isohexyl.

Alkenyl, haloalkenyl, alkynyl and haloalkynyl are straight-chain or branched and in each case contain two or preferably one unsaturated carbon-carbon bond(s). The double or triple bonds of this substituent are preferably separated from the remaining part of the compound of the formula (A) by at least one saturated carbon atom. Examples are allyl, methallyl, but-2-enyl, but-3-enyl, propargyl, but-2-ynyl and but-3-ynyl.

Halogen-substituted carbon-containing groups and compounds, such as haloalkyl, haloalkylthio, haloalkoxy, halocyclopropyl, haloalkenyl, haloalkynyl, haloallyloxy and haloallylthio, can be partly halogenated or perhalogenated, and in the case of multiple halogenation the halogen substituents can be identical or different. Examples of haloalkyl - as a group per se and as a structural element of other groups and compounds, such as of haloalkylthio and haloalkoxy - are methyl which is mono- to trisubstituted by fluorine, chlorine and/or bromine, such as CHF_2 or CF_3 ; ethyl which is mono- to pentasubstituted by fluorine, chlorine and/or bromine, such as CH_2CF_3 , CF_2CF_3 , CF_2CCl_3 , CF_2CHCl_2 , CF_2CHF_2 , CF_2CFCl_2 , CF_2CHBr_2 , CF_2CHClF , CF_2CHBrF or CClFCHClF ; propyl or isopropyl which are mono- to heptasubsti-

tuted by fluorine, chlorine and/or bromine, such as $\text{CH}_2\text{CHBrCH}_2\text{Br}$, $\text{CF}_2\text{CHFCH}_2\text{F}$, $\text{CH}_2\text{CF}_2\text{CF}_3$, $\text{CF}_2\text{CF}_2\text{CF}_3$ or $\text{CH}(\text{CF}_3)_2$; and butyl or one of its isomers which are mono- to nonasubstituted by fluorine, chlorine and/or bromine, such as $\text{CF}(\text{CF}_3)\text{CHFCH}_2\text{F}$, $\text{CF}_2(\text{CF}_3)_2\text{CF}_3$ or $\text{CH}_2(\text{CF}_3)_2\text{CF}_3$. Examples of haloalkenyl are 2,2-difluoroethen-1-yl, 2,2-dichloroethen-1-yl, 2-chloroprop-1-en-3-yl, 2,3-dichloroprop-1-en-3-yl and 2,3-dibromoprop-1-en-3-yl. Examples of haloalkynyl are 2-chloroprop-1-yn-3-yl, 2,3-dichloroprop-1-yn-3-yl and 2,3-dibromoprop-1-yn-3-yl. Examples of halocyclopropyl are 2-chlorocyclopropyl, 2,2-difluorocyclopropyl and 2-chloro-2-fluoro-cyclopropyl. Examples of haloalkyloxy are 2-chloroprop-1-en-3-yloxy, 2,3-dichloroprop-1-en-3-yloxy and 2,3-dibromoprop-1-en-3-yloxy. Examples of haloalkylthio are 2-chloroprop-1-en-3-ylthio, 2,3-dichloroprop-1-en-3-ylthio and 2,3-dibromoprop-1-en-3-ylthio.

In phenylalkyl, an alkyl group bonded to the remaining part of the compound of the formula (A) is substituted by a phenyl group, the alkyl group preferably being straight-chain and the phenyl group preferably being bonded to the alkyl group in a position higher than the α -position, in particular in the ω -position; examples are benzyl, 2-phenylethyl and 4-phenylbutyl.

Particularly preferred compounds of the formula (A) are those in which

- (1) R is hydrogen, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_3\text{-C}_6$ cycloalkyl, $\text{C}_2\text{-C}_6$ alkenyl or $\text{C}_2\text{-C}_6$ alkynyl, in particular H or CH_3 ;
- (2) the cyclic base skeleton of A contains 2 to 4, preferably conjugated, double bonds, preferably contains 2, preferably conjugated double bonds, and in particular has aromatic character,
- (3) the cyclic base skeleton of A contains 1 up to and including 4, in particular 1 up to and including 3, especially 1 or 2, heteroatoms, particularly preferably 2 heteroatoms;
- (4) the cyclic base skeleton of A contains 1, 2 or 3 heteroatoms chosen from the group consisting of oxygen, sulfur and nitrogen, not more than one of the heteroatoms contained in the cyclic base skeleton being an oxygen or sulfur atom, preferably at least one nitrogen atom;

(5) a compound of the formula (A), in which A is mono- or disubstituted by substituents chosen from the group consisting of halogen and C_1 - C_3 alkyl, in particular by halogen, especially by chlorine;

(6) a compound of the formula (A) in which the cyclic base skeleton of A is a pyridyl, 1-oxdopyridinio or thiazolyl group, preferably the cyclic base skeleton of A is a pyrid-3-yl-, 1-oxido-3-pyridinio or thiazol-5-yl group,

in particular A is a pyrid-3-yl, 2-halopyrid-5-yl, 2,3-dihalopyrid-5-yl, 2- C_1 - C_3 alkylpyrid-5-yl, 1-oxido-3-pyridinio, 2-halo-1-oxido-5-pyridinio, 2,3-dihalo-1-oxido-5-pyridinio or 2-halothiazol-5-yl group,

A is especially a pyrid-3-yl, 2-halopyrid-5-yl, 2-halo-1-oxido-5-pyridinio or 2-halothiazol-5-yl group,

preferably A is a 2-chloropyrid-5-yl, 2-methylpyrid-5-yl, 1-oxido-3-pyridinio, 2-chloro-1-oxido-5-pyridinio, 2,3-dichloro-1-oxido-5-pyridinio or 2-chlorothiazol-5-yl group,

A is especially a pyrid-3-yl, 2-chloropyrid-5-yl, 2-chloro-1-oxido-5-pyridinio or 2-chlorothiazol-5-yl group,

In particular A is a 2-chloropyrid-5-yl or, preferably, 2-chlorothiazol-5-yl group

(7) a compound of the formula (A), in which X is $N-NO_2$;

(8) a compound of the formula (A), in which A is a 2-chlorothiazol-5-yl or 2-chloropyrid-5-yl group, R is C_1 - C_4 alkyl and X is $N-NO_2$.

Compounds of the formula (A) which are named as preferred in the context of the invention are

- (A.1) (2-chloropyrid-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine;
- (A.2) (2-chlorothiazol-5-ylmethyl)-3-ethyl-4-nitroimino-perhydro-1,3,5-oxadiazine;
- (A.3) 3-methyl-4-nitroimino-5-(1-oxido-3-pyridinylmethyl)-perhydro-1,3,5-oxadiazine;
- (A.4) (2-chloro-1-oxido-5-pyridinylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine;
- (A.5) (2-chlorothiazol-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine;
- (A.6) 3-methyl-5-(2-methylpyrid-5-ylmethyl)-4-nitroimino-perhydro-1,3,5-oxadiazine;
- (A.7) (2-chloropyrid-5-ylmethyl)-4-nitroimino-perhydro-1,3,5-oxadiazine;
- (A.8) (2-chlorothiazol-5-ylmethyl)-4-nitroimino-perhydro-1,3,5-oxadiazine, or

(A.9) (2-chloropyrid-5-ylmethyl)-3-ethyl-4-nitroimino-perhydro-1,3,5-oxadiazine.

5-(2-chlorothiazol-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine is especially preferred in the context of the invention as the mixing partner of the formula (A). A composition which, in addition to the compound of the formula (A), also comprises only one further compound (I) to (CLXXXIV) having a pesticidal action is also preferred. Compositions which comprise pirimicarb in addition to a compound of the formula (A) are furthermore preferred. Compositions which comprise pyriproxyfen, flupronil, endosulfan or buprofezin in addition to a compound of the formula (A) are likewise preferred.

The active compound combination according to the invention preferably comprises the active compound of the formula (A) and one of the active compounds (I) to (CLXXXIV) in a mixing ratio of 100:1 to 1:6000, in particular 1:50 to 50:1, in particular in a ratio of between 1:20 and 20:1, in particular between 10:1 and 1:10, especially between 5:1 and 1:5, particularly preferably between 2:1 and 1:2, and also preferably between 4:1 and 2:1, especially in the ratio of 1:1, or 5:1, or 5:2, or 5:3, or 5:4, or 4:1, or 4:2, or 4:3, or 3:1, or 3:2, or 2:1, or 1:5, or 2:5, or 3:5, or 4:5, or 1:4, or 2:4, or 3:4, or 1:3, or 2:3, or 1:2, or, 1:600, or 1:300, or 1:150, or 1:35, or 2:35, or 4:35, or 1:75, or 2:75, or 4:75, or 1:6000, or 1:3000, or 1:1500, or 1:350, or 2:350, or 4:350, or 1:750, or 2:750, or 4:750. These ratios are understood as meaning weight ratios on the one hand, and also molar ratios on the other hand.

It has now been found, surprisingly, that the combination of the active compound of the formula (A) or of one of its salts with one of the active compounds (I) to (CLXXXIV) not only causes an additive increase in the action spectrum on the pests to be controlled, which is to be expected in principle, but that it achieves a synergistic effect which extends the action limits of both preparations under two aspects:

On the one hand, the rates of application of the compound of the formula (A) and of the individual compounds (I) to (CLXXXIV) are lowered for the same good action. On the other hand, the combined mixture also still has a high degree of pest control where the two individual substances have become completely inactive in the range of excessively low rates of application. This allows on the one hand a considerable extension to the spectrum of pests which can be controlled and on the other hand an increase in application reliability.

In addition to the actual synergistic action in respect of pesticidal activity, however, the compositions according to the invention also additionally have further surprising advantages which can likewise be described as synergistic in a broadened sense: thus, for example, it is possible to control pests which cannot be controlled or sufficiently effectively controlled with the individual compounds (A) or (I) to (CLXXXIV), and the compositions according to the invention show a better toleration by plants, i.e., for example, a reduced phytotoxicity, than the individual compounds (A) and (I) to (CLXXXIV). The insects can furthermore be controlled in their various stages of development, which sometimes is not the case with the individual compounds (A) and (I) to (CLXXXIV), since these compounds can be used, for example, only as adulticides or only as larvicides against quite specific larval stages. In addition, combinations of the compound (A) with certain compounds (I) to (CLXXXIV) show more favourable properties during grinding, mixing, storage and also spraying.

The compositions according to the invention are valuable preventively and/or curatively even at low rates of concentration in the field of pest control, while being tolerated by warm-blooded animals, fishes and plants, and have a very favourable biocidal spectrum. The compositions according to the invention are active against all or individual stages of development of normally sensitive and also resistant animal pests, such as insects and representatives of the order Acarina. The insecticidal and/or acaricidal action of the compositions according to the invention can manifest itself here directly, i.e. in a destruction of the pests, which occurs immediately or only after some time, for example during moulting, or indirectly, for example in a reduced oviposition and/or hatching rate, the good action corresponding to a rate of destruction (mortality) of at least 50 to 60%.

The animal pests include, for example:
from the order Lepidoptera

Acleris spp., *Adoxophyes* spp., *Aegeria* spp., *Agrotis* spp., *Alabama argillaceae*, *Amylois* spp., *Anticarsia gemmatilis*, *Archips* spp., *Argyrotaenia* spp., *Autographa* spp., *Busseola fusca*, *Cadra cautella*, *Carposina nipponensis*, *Chilo* spp., *Choristoneura* spp., *Clysia ambiguella*, *Cnaphalocrocis* spp., *Cnephasia* spp., *Cochylis* spp., *Coleophora* spp., *Crocidolomia binotalis*, *Cryptophlebia leucotreta*, *Cydia* spp., *Diatraea* spp., *Diparopsis castanea*, *Earlas* spp., *Ephesia* spp., *Eucosma* spp., *Eupoecilia ambiguella*, *Euprocitis* spp., *Euxoa* spp., *Grapholita* spp., *Hedya nubiferana*, *Heliothis* spp., *Hellula* spp., *Hyphantria cunea*, *Kelleria*

lycopersicella, *Leucoptera scitella*, *Lithocolletis* spp., *Lobesia botrana*, *Lymantria* spp., *Lyonetia* spp., *Malacosoma* spp., *Mamestra brassicae*, *Manduca sexta*, *Operophtera* spp., *Ostrinia nubilalis*, *Pammene* spp., *Pandemis* spp., *Panolis flammea*, *Pectinophora gossypiella*, *Phthorimaea operculella*, *Pieris rapae*, *Pieris* spp., *Plutella xylostella*, *Prays* spp., *Scirpophaga* spp., *Sesamia* spp., *Sparganothis* spp., *Spodoptera* spp., *Synanthedon* spp., *Thaumetopoea* spp., *Tortrix* spp., *Trichoplusia ni* and *Yponomeuta* spp.;

from the order Coleoptera, for example

Agriotes spp., *Anthonomus* spp., *Atomaria linearis*, *Chaetocnema tibialis*, *Cosmopolites* spp., *Curculio* spp., *Dermestes* spp., *Diabrotica* spp., *Epilachna* spp., *Eremnus* spp., *Leptinotarsa decemlineata*, *Lissorhoptrus* spp., *Melolontha* spp., *Oryzaephilus* spp., *Otiorynchus* spp., *Phlyctinus* spp., *Popillia* spp., *Psyllodes* spp., *Rhizopertha* spp., *Scarabeidae*, *Sitophilus* spp., *Sitotroga* spp., *Tenebrio* spp., *Tribolium* spp. and *Trogoderma* spp.;

from the order Orthoptera, for example

Blatta spp., *Blattella* spp., *Gryllotalpa* spp., *Leucophaea maderae*, *Locusta* spp., *Periplaneta* spp. and *Schistocerca* spp.;

from the order Isoptera, for example

Reticulitermes spp.;

from the order Psocoptera, for example

Liposcelis spp.;

from the order Anoplura, for example

Haematopinus spp., *Linognathus* spp., *Pediculus* spp., *Pemphigus* spp. and *Phylloxera* spp.;

from the order Mallophaga, for example

Damalinea spp. and *Trichodectes* spp.;

from the order Thysanoptera, for example

Frankliniella spp., *Hercinothrips* spp., *Taeniothrips* spp., *Thrips palmi*, *Thrips tabaci* and *Scirtothrips aurantii*;

from the order Heteroptera, for example

Cimex spp., *Distantiella theobroma*, *Dysdercus* spp., *Euchistus* spp., *Eurygaster* spp., *Leptocoris* spp., *Nezara* spp., *Piesma* spp., *Rhodnius* spp., *Sahlbergella singularis*, *Scotinophara* spp. and *Triatoma* spp.;

from the order Homoptera, for example

Aleurothrix floccosus, *Aleyrodes brassicae*, *Aonidiella* spp., *Aphididae*, *Aphis* spp., *Aspidiotus* spp., *Bemisia tabaci*, *Ceroplaster* spp., *Chrysomphalus aonidium*, *Chrysomphalus dictyospermi*, *Coccus hesperidum*, *Empoasca* spp., *Eriosoma lanigerum*, *Erythroneura* spp., *Gascardia* spp., *Laodelphax* spp., *Lecanium corni*, *Lepidosaphes* spp., *Macrosiphus* spp., *Myzus* spp., *Nephotettix* spp., *Nilaparvata* spp., *Paratoria* spp., *Pemphigus* spp., *Planococcus* spp., *Pseudaulacaspis* spp., *Pseudococcus* spp., *Psylla* spp., *Pulvinaria aethiopica*, *Quadraspidotus* spp., *Rhopalosiphum* spp., *Saissetia* spp., *Scaphoideus* spp., *Schizaphis* spp., *Sitobion* spp., *Trialeurodes vaporariorum*, *Trioxa erytrae* and *Unaspis citri*;

from the order Hymenoptera, for example

Acromyrmex, *Atta* spp., *Cephus* spp., *Diprion* spp., *Diprionidae*, *Gilpinia polytoma*, *Hoplomampa* spp., *Lasius* spp., *Monomorium pharaonis*, *Neodiprion* spp., *Solenopsis* spp. and *Vespa* spp.;

from the order Diptera, for example

Aedes spp., *Antherigona soccata*, *Bibio hortulanus*, *Calliphora erythrocephala*, *Ceratitis* spp., *Chrysomya* spp., *Culex* spp., *Cuterebra* spp., *Dacus* spp., *Drosophila melanogaster*, *Fannia* spp., *Gastrophilus* spp., *Glossina* spp., *Hypoderma* spp., *Hypobosca* spp., *Liriomyza* spp., *Lucilia* spp., *Melanagromyza* spp., *Musca* spp., *Oestrus* spp., *Orseolia* spp., *Oscinella frit*, *Pegomyia hyoscyami*, *Phorbia* spp., *Rhagoletis pomonella*, *Sciara* spp., *Stomoxys* spp., *Tabanus* spp., *Tannia* spp. and *Tipula* spp.;

from the order Siphonaptera, for example

Ceratophyllus spp. and *Xenopsylla cheopis*;

from the order Thysanura, for example

Lepisma saccharina and

from the order Acarina, for example

Acarus siro, *Aceria sheldoni*, *Aculus schlechtendali*, *Amblyomma* spp., *Argas* spp., *Boophilus* spp., *Brevipalpus* spp., *Bryobia praetiosa*, *Calipitimerus* spp., *Chorioptes* spp., *Dermanyssus gallinae*, *Eotetranychus carpini*, *Eriophyes* spp., *Hyalomma* spp., *Ixodes* spp., *Olygonychus pratensis*, *Ornithodoros* spp., *Panonychus* spp., *Phyllocoptura oleivora*, *Polyphagotarsonemus latus*, *Psoroptes* spp., *Rhipicephalus* spp., *Rhizoglyphus* spp., *Sarcoptes* spp., *Tarsonemus* spp. and *Tetranychus* spp..

Using the active compound mixtures according to the invention, in particular pests of the type mentioned which occur on plants, especially useful plants and ornamentals in agricultu-

re, in horticulture and in forestry, or on parts, such as fruit, blossom, foliage, stems, tubers, or roots, of such plants can be controlled, i.e. checked or destroyed, and in some cases parts of plants which additionally grow later are also still protected from these pests.

The pesticidal mixture according to the invention can advantageously be employed for pest control in cereals, such as maize or sorghum; in fruit, for example pome, stone and soft fruit, such as apples, pears, plums, peaches, almonds, cherries or berries, for example strawberries, raspberries and blackberries; in leguminous plants, such as beans, lentils, peas or soya; in oil-bearing crops, such as oilseed rape, mustard, poppy seed, olives, sunflower, coconut, castor, cacao or groundnuts; in gourds, such as pumpkins, cucumbers or melons; in fibre plants, such as cotton, flax, hemp or jute; in citrus fruits, such as oranges, lemons, grapefruits or mandarins; in vegetables, such as spinach, lettuce, asparagus, cabbage varieties, carrots, onions, tomatoes, potatoes or capsicum; in lauraceous plants, such as avocado, cinnamonum, camphor; or in tobacco, nuts, coffee, aubergines, sugar cane, tea, pepper, vines, hops, musaceous plants, natural rubber plants or ornamentals, in particular in maize, sorghum, pome and stone fruits, leguminous plants, cucurbits, cotton, citrus fruits, vegetables, aubergines, vines, hops or ornamentals, especially in maize, sorghum, apples, pears, plums, peaches, beans, peas, soya, olives, sunflower, coconut, cacao, groundnuts, cucumbers, pumpkins, citrus fruits, cabbage varieties, tomatoes, potatoes, vines or cotton, particularly preferably in vines, citrus fruits, apples, pears, tomatoes and cotton.

Other fields of use of the active compound mixtures according to the invention are protection of stored products and stocks and of material, and in the hygiene sector, in particular the protection of domestic animals and productive livestock against pests of the type mentioned.

Depending on the aims to be achieved and the given circumstances, the pesticides according to the invention are emulsifiable concentrates, suspension concentrates, directly sprayable or dilutable solutions, spreadable pastes, dilute emulsions, sprayable powders, soluble powders, dispersible powders, wettable powders, dusts, granules or encapsulations in polymeric substances which comprise the compound of the formula (A) or one of its salts and one of the other active compounds (I) to (CLXXXIV) according to the invention.

The active compounds are employed in these compositions in a pure form, the solid active compounds, for example, being employed in a specific particle size, or, preferably, together with - at least - one of the auxiliaries conventionally used in the art of formulation, such as extenders, for example solvents or solid carriers, or such as surface-active compounds (surfactants).

Solvents are, for example: non-hydrogenated or partly hydrogenated aromatic hydrocarbons, preferably fractions C₈ to C₁₂ of alkylbenzenes, such as xylene mixtures, alkylated naphthalenes or tetrahydronaphthalene, aliphatic or cycloaliphatic hydrocarbons, such as paraffins or cyclohexane, alcohols, such as ethanol, propanol or butanol, glycols and ethers and esters thereof, such as propylene glycol, dipropylene glycol ether, ethylene glycol or ethylene glycol monomethyl or -ethyl ether, ketones, such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents, such as N-methylpyrrolid-2-one, dimethyl sulfoxide or N,N-dimethylformamide, water, non-epoxidized or epoxidized plant oils, such as non-epoxidized or epoxidized rapeseed, castor, coconut or soya oil, and silicone oils.

Solid carriers, for example for dusts and dispersible powders, which are as a rule used are natural rock powders, such as calcite, talc, kaolin, montmorillonite or attapulgite. Highly disperse silicic acids or highly disperse absorbent polymers can also be added to improve the physical properties. Granular, adsorptive granule carriers are porous types, such as pumice, crushed brick, sepiolite or bentonite, and non-adsorptive carrier materials are calcite or sand. A large number of granulated materials of inorganic or organic nature, in particular dolomite or comminuted plant residues, can furthermore be used.

Surface-active compounds are, depending on the nature of the active compound to be formulated, nonionic, cationic and/or anionic surfactants or surfactant mixtures having good emulsifying, dispersing and wetting properties. The surfactants listed below are to be regarded only as examples here; many other surfactants which are conventionally used in the art of formulation and are suitable according to the invention are described in the relevant literature.

Nonionic surfactants are, in particular, polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, which can contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols. Water-soluble adducts,

containing 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups, of polyethylene oxide on polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol having 1 to 10 carbon atoms in the alkyl chain are furthermore suitable. The compounds mentioned usually comprise 1 to 5 ethylene glycol units per propylene glycol unit. Examples are nonylphenol-polyethoxyethanols, castor oil polyglycol ether, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Fatty acid esters of polyoxyethylene-sorbitan, such as polyoxyethylene-sorbitan trioleate, are furthermore possible.

Cationic surfactants are, in particular, quaternary ammonium salts which contain, as substituents, at least one alkyl radical having 8 to 22 C atoms and, as further substituents, lower, non-halogenated or halogenated alkyl, benzyl or lower hydroxy alkyl radicals. The salts are preferably in the form of halides, methyl-sulfates or ethyl-sulfates. Examples are stearyltrimethylammonium chloride and benzyl(2-chloroethyl)ethylammonium bromide.

Suitable inorganic surfactants can be both water-soluble soaps and water-soluble synthetic surface-active compounds. Suitable soaps are the alkali metal, alkaline earth metal and substituted and unsubstituted ammonium salts of higher fatty acids (C_{10} - C_{22}), such as the sodium or potassium salts of oleic or stearic acid, or of naturally occurring fatty acid mixtures, which can be obtained, for example, from coconut oil or tall oil; and furthermore also the fatty acid methyl-taurine salts. However, synthetic surfactants are more frequently used, in particular fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates. The fatty sulfonates and sulfates are as a rule in the form of alkali metal, alkaline earth metal or substituted or unsubstituted ammonium salts, and in general contain an alkyl radical having 8 to 22 C atoms, alkyl also including the alkyl moiety of acyl radicals; examples are the sodium or calcium salt of ligninsulfonic acid, of dodecylsulfuric acid ester or of a fatty alcohol sulfate mixture prepared from naturally occurring fatty acids. These also include the salts of sulfuric acid esters and sulfonic acids of fatty alcohol-ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain two sulfonic acid groups and one fatty acid radical having about 8 to 22 C atoms. Alkylarylsulfonates are, for example, the sodium, calcium or triethanolammonium salts of dodecylbenzenesulfonic acid, of dibutylinaphthalenesulfonic acid or of a naphthalenesulfonic acid-formaldehyde condensati-

on product. Corresponding phosphates, such as salts of the phosphoric acid ester of a p-nonylphenol-(4-14)-ethylene oxide adduct or phospholipids, are furthermore also suitable.

The compositions as a rule comprise 0.1 to 99%, in particular 0.1 to 95%, of a mixture of the active compound of the formula (A) with one of the active compounds (I) to (CLXXXIV), and 1 to 99.9%, in particular 5 to 99.9%, of - at least - one solid or liquid auxiliary, where as a rule 0 to 25%, in particular 0.1 to 20%, of the compositions can be surfactants (% is in each case per cent by weight). While concentrated compositions are rather preferred as commercial goods, the end user as a rule uses dilute compositions which have considerably lower active compound concentrations. Preferred compositions have, in particular, the following composition (% = per cent by weight):

Emulsifiable concentrates:

Active compound mixture	1 to 90%, preferably 5 to 20%
Surfactant:	1 to 30%, preferably 10 to 20 %
Solvent:	5 to 98%, preferably 70 to 85%

Dusts:

Active compound mixture:	0.1 to 10%, preferably 0.1 to 1%
Solid carrier:	99.9 to 90%, preferably 99.9 to 99%

Suspension concentrates:

Active compound mixture:	5 to 75%, preferably 10 to 50%
Water:	94 to 24%, preferably 88 to 30%
Surfactant:	1 to 40%, preferably 2 to 30%

Wettable powders:

Active compound mixture:	0.5 to 90%, preferably 1 to 80%
Surfactant:	0.5 to 20%, preferably 1 to 15%
Solid carrier:	5 to 99%, preferably 15 to 98%

Granules:

Active compound mixture:	0.5 to 30%, preferably 3 to 15%
Solid carrier:	99.5 to 70%, preferably 97 to 85%

The compositions according to the invention can also comprise other solid or liquid auxiliaries, such as, stabilizers, for example non-epoxidized or epoxidized plant oils (for example epoxidized coconut oil, rape oil or soya oil), defoamers, for example silicone oil, preservatives, viscosity regulators, binders and/or tackifiers, as well as fertilizers or other active compounds for achieving specific effects, for example bactericides, fungicides, nematocides, molluscicides or herbicides.

The compositions according to the invention are prepared in a known manner, in the absence of auxiliaries, for example, by grinding, sieving and/or pressing a solid active compound or active compound mixture, for example to a particular particle size, and in the presence of at least one auxiliary, for example, by intimate mixing and/or grinding of the active compound or active compound mixture with the auxiliary or auxiliaries. The invention therefore also relates to the process for the preparation of the compositions.

Mixtures of a compound of the formula (A) with one or more of the compounds (I) to (CLXXXIV) are preferably employed with the auxiliaries conventionally used in the art of formulation, and are therefore processed, for example, to emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts and granules, and also to encapsulations in, for example, polymeric substances, in a known manner. The methods of application, such as spraying, atomizing, dusting, wetting, scattering or pouring are chosen, as is the nature of the composition, according to the aims to be achieved and the given circumstances.

The invention furthermore relates to the methods of application for the compositions, i.e. the methods for controlling pests of the type mentioned, such as spraying, atomizing, dusting, spreading, dressing, scattering or pouring, to be chosen according to the aims to be achieved and the given circumstances, and the use of the compositions for controlling pests of the type mentioned. Typical rates of concentration here are between 0.1 and 1000 ppm, preferably between 0.1 and 500 ppm, of active compound. The rate of application can vary within wide limits and depends on the nature of the soil, the nature of the application, (leaf application; seed dressing, application in the seed furrow), the crop plant, the pest to be controlled, the particular climatic circumstances which prevail and other factors determined by the nature of the application, the time of application and the target crop. The rates of

application per hectare are in general 1 to 2000 g of active compound per hectare, in particular 10 to 1000 g/ha, preferably 20 to 600 g/ha.

A preferred method of application in the field of crop protection is application to the foliage of the plants (leaf application), where the frequency of application and rate of application can be chosen according to the risk of infestation by the particular pest. However, the active compound can also enter the plants via the root system (systemic action) by impregnating the locus of the plants with a liquid composition or introducing the active compounds in solid form into the locus of the plants, for example into the soil, for example in the form of granules (soil application). In paddy rice crops, such granules can be metered onto the flooded rice field.

The compositions according to the invention are also suitable for the protection of plant propagation material, for example seeds, such as fruit, tubers, or grain, or plant seedlings, against animal pests. The propagation material can be treated with the composition before being brought out, for example seed can be dressed before sowing. The active compounds according to the invention can also be applied to the seed grains (coating) either by impregnating the grains in a liquid composition or coating them with a solid composition. The composition can also be applied to the site where the propagation material is brought out, during broadcasting, for example into the seed furrow during sowing. The invention furthermore relates to the treatment methods for plant propagation material and the plant propagation material treated in this way.

The following examples serve to illustrate the invention. They do not limit the invention.

Formulation examples (% = % by weight, active compound ratios = weight ratios)

<u>Example F1: Emulsion concentrates</u>	a)	b)	c)
Active compound mixture (Compound (A) :			
Compound (I) to (CLXXXIV) = 1 : 1)	25 %	40 %	50 %
Ca dodecylbenzenesulfonate	5 %	8 %	6 %
Castor oil polyethylene glycol ether (36 mol of EO)	5 %		
Tributylphenolpolyethylene glycol ether (30 mol of EO)		12 %	4 %
Cyclohexanone		15 %	20 %
Xylene mixture	65 %	25 %	20 %

EO is the degree of ethoxylation of castor oil or tributylphenol.

Emulsions of any desired concentration can be prepared from such concentrates by dilution with water.

Example F2: Solutions

	a)	b)	c)	d)
Active compound mixture (Compound (A) :				
Compound (I) to (CLXXXIV) = 1 : 3)	80 %	10 %	5 %	95 %
Ethylene glycol monomethyl ether		20 %		
Polyethylene glycol molecular wt. 400	-	70 %		
N-methyl-2-pyrrolidone	20 %	-		
Epoxidized coconut oil			1 %	5 %
Benzine (boiling limits 160-190°C)			94 %	

The solutions are suitable for use in the form of tiny drops.

Example F3: Granules

	a)	b)	c)	d)
Active compound mixture (Compound (A) :				
Compound (I) to (CLXXXIV) = 3 : 1)	5 %	10 %	8 %	21 %
Kaolin	94 %		79 %	54 %
Highly disperse silicic acid	1 %		13 %	7 %
Attapulgit		90 %		18 %

The active compounds are dissolved together in methylene chloride, the solution is sprayed onto the carrier and the solvent is then evaporated off in vacuo.

Example F4: Dusts

	a)	b)
Active compound mixture (1 : 1)	2 %	5 %
Highly disperse silicic acid	1 %	5 %
Talc	97 %	
Kaolin		90 %

Intimate mixing of the carriers with the active compounds gives ready-to-use dusts.

Example F5: Wettable powders

	a	b)	c)
Active compound mixture (Compound (A) :			
Compound (I) to (CLXXXIV) = 4 : 1)	25 %	50 %	75 %
Sodium ligninsulfonate	5 %	5 %	
Sodium lauryl sulfate	3 %		5 %
Sodium diisobutylphenyl naphthalene-sulfonate		6 %	10 %
Octylphenol polyethylene glycol-ether (7-8 mol of EO)		2 %	-
Highly disperse silicic acid	5 %	10 %	10 %
Kaolin	62 %	27 %	-

The active compounds are mixed with the additives and ground thoroughly in a suitable mill. Wettable powders which can be diluted with water to give suspensions of any desired concentration are obtained.

Example F6: Emulsion concentrate

Active compound mixture (1 : 2)	10 %
Octylphenol polyethylene glycol ether	
(4-5 mol of EO)	3 %
Calcium dodecylbenzenesulfonate	3 %
Castor oil polyglycol ether	
(36 mol of EO)	4 %
Cyclohexanone	30 %
Xylene mixture	50 %

Emulsions of any desired concentration can be prepared from this concentrate by dilution with water.

Example F7: Dusts

	a)	b)
Active compound mixture (Compound (A) :		
Compound (I) to (CLXXXIV) = 2 : 5)	5%	8 %
Talc	95 %	-
Kaolin		92 %

Ready-to-use dusts are obtained by mixing the active compounds with the carrier and grinding the mixture on a suitable mill.

Example F8: Extruded granules

Active compound mixture (2 : 1)	10 %
Sodium ligninsulfonate	2 %
Carboxymethylcellulose	1 %
Kaolin	87 %

The active compounds are mixed with the additives and the mixture is ground and moistened with water. This mixture is extruded, granulated and then dried in a stream of air.

Example F9: Coated granules

Active compound mixture (1 : 1)	3 %
Polyethylene glycol (molecular wt. 200)	3 %
Kaolin	94 %

The finely ground active compounds are applied uniformly to the kaolin, which is moistened with polyethylene glycol, in a mixer. Dust-free coated granules are obtained in this way.

Example F10: Suspension concentrate

Active compound mixture (1 : 1)	40 %
Ethylene glycol	10 %
Nonylphenol polyethylene glycol ether (15 mol of EO)	6 %
Sodium ligninsulfonate	10 %
Carboxymethylcellulose	1 %
37% aqueous formaldehyde solution	0,2 %
Silicone oil in the form of a 75% aqueous emulsion	0.8 %
Water	32 %

The finely ground active compounds are mixed intimately with the additives. A suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water is thus obtained.

It is often more practical to formulate the active compound of the formula (A) and one of the mixing partners (I) to (CLXXXIV) individually and then to bring them together in the applicator in the desired mixing ratio as "tank mixing" in the water only shortly before application.

Biological Examples (% = per cent by weight, unless stated otherwise)

A synergistic effect is always present if the action EA of the combination of an active compound of the formula (A) with one of the active compounds (I) to (CLXXXIV) is greater than the sum of the action of the active compounds applied individually:

$$EA_1 > X + Y \quad (B)$$

However, the pesticidal action EA to be expected for a given combination of two pesticides can also be calculated as follows (cf. COLBY, S.R., "Calculating synergistic and antagonistic response of herbicide combinations", Weeds 15, Pages 20-22, 1967).

In this equation:

$$EA_2 = X + \frac{Y(100 - X)}{100}$$

X = Per cent mortality on treatment with the compound of the formula (A) at a rate of application of p kg per hectare compared with the untreated control (= 0 %).

Y = Per cent mortality on treatment with a compound (I) to (CLXXXIV) at a rate of application of q kg per hectare compared with the untreated control.

EA = Expected pesticidal action (per cent mortality compared with the untreated control) after treatment with the compound of the formula (A) and a compound (I) to (CLXXXIV) at a rate of application of p + q kg of active compound per hectare.

If the action actually observed is greater than the expected value EA, synergism exists.

Example B1: Action against Bemisia tabaci

Dwarf bean plants are placed in gauze cages and populated with adults of Bemisia tabaci. After oviposition has taken place, all the adults are removed. 10 days later, the plants with the nymphs on them are sprayed with an aqueous suspension spray liquor comprising 50 ppm of the active compound mixture. After a further 14 days, the percentage hatching of the eggs is evaluated in comparison with untreated control batches.

In this test, the combinations of an active compound of the formula (A) with one of the active compounds (I) to (CLXXXIV) show a synergistic effect. In particular, a suspension spray liquor which comprises 40 ppm of the compound (A.5) and 10 ppm of the compound (II) shows an activity of over 80%.

Example B2: Action against *Spodoptera littoralis* caterpillars

Young soya plants are sprayed with an aqueous emulsion spray liquor comprising 360 ppm of the active compound mixture. After the spray coating has dried on, the soya plants are populated with 10 caterpillars of the third stage of *Spodoptera littoralis* and placed in a plastic container. Evaluation takes place 3 days later. The percentage reduction in the population and the percentage reduction in feeding damage (% action) are determined from comparison of the number of dead caterpillars and of the feeding damage on the treated plants to those on the untreated plants.

In this test, combinations of an active compound of the formula (A) with one of the active compounds (I) to (CLXXXIV) show a synergistic effect. In particular, a suspension spray liquor which comprises 200 ppm of the compound (A.2) and 160 ppm of the compound (XXIX) and a suspension spray liquor which comprises 120 ppm of the compound (A) and 240 ppm of the compound (XXIV) show an activity of over 80%.

Example B3: Ovizidal action on *Lobesia botrana*

Lobesia botrana eggs deposited on filter paper are immersed for a short time in an acetone-aqueous test solution comprising 400 ppm of the active compound mixture to be tested. After the test solution has dried on, the eggs are incubated in Petri dishes. After 6 days, the percentage hatching of the eggs is evaluated in comparison with untreated control batches (% reduction in hatching).

In this test, combinations of an active compound of the formula (A) with one of the active compounds (I) to (CLXXXIV) show a synergistic effect. In particular, a suspension spray liquor which comprises 300 ppm of the compound (A.5) and 100 ppm of the compound (III) and a suspension spray liquor which comprise 200 ppm of the compound (A.2) and 200 ppm of the compound (LVII) show an activity of over 80%.

Example B4: Ovizidal action on *Heliothis virescens*

Heliothis virescens eggs deposited on filter paper are immersed for a short time in an acetone-aqueous test solution comprising 400 ppm of the active compound mixture to be tested. After the test solution has dried on, the eggs are incubated in Petri dishes. After 6 days, the percentage hatching of the eggs is evaluated in comparison with untreated control batches (% reduction in hatching).

In this test, combinations of an active compound of the formula (A) with one of the active compounds (I) to (CLXXXIV) show a synergistic effect. In particular, a suspension spray liquor which comprises 240 ppm of the compound (A.1) and 160 ppm of the compound (I) and a suspension spray liquor which comprise 100 ppm of the compound (A.5) and 300 ppm of the compound (I) show an activity of over 80%.

Example B5: Action against *Plutella xylostella* caterpillars

Young cabbage plants are sprayed with an aqueous emulsion spray liquor which comprises 440 ppm of the active compound. After the spray coating has dried on, the cabbage plants are populated with ten caterpillars of the third stage of *Plutella xylostella* and placed in a plastic container. The evaluation takes place 3 days later. The percentage reduction in population and percentage reduction in feeding damage (% action) are determined from the comparison of the number of dead caterpillars and of the feeding damage on the treated plants to those on the untreated plants.

In this test, combinations of an active compound of the formula (A) with one of the active compounds (I) to (CLXXXIV) show a synergistic effect. In particular, a suspension spray liquor which comprises 40 ppm of the compound (A.5) and 400 ppm of the compound (XI) and a suspension spray liquor which comprises 220 ppm of the compound (A.7) and 220 ppm of the compound (L) show an activity of over 80%.

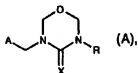
Example B6: Action against *Myzus persicae*

Pea seedlings are infected with *Myzus persicae*, subsequently sprayed with a spray liquor comprising 400 ppm of the active compound and incubated at 20°C. An evaluation takes place 3 and 6 days later. The percentage reduction in the population (% action) is determined from the comparison of the number of dead aphids on the treated plants to that on the untreated plants.

In this test, combinations of an active compound of the formula (A) with one of the active compounds (I) to (CLXXXIV) show a synergistic effect. In particular, a suspension spray liquor which comprises 1 ppm of the compound (A.5) and 40 ppm of pirimicarb and a suspension spray liquor which comprises 0.2 ppm of the compound (A.5) and 75 ppm of pirimicarb show an activity of over 80%.

WHAT IS CLAIMED IS:

1. A composition for controlling insects or representatives of the order Acarina, which comprises a combination of variable amounts of one or more compounds of the formula



in which

A is an unsubstituted or, depending on the possibility of substitution on the ring system, mono- to tetrasubstituted, aromatic or non-aromatic monocyclic or bicyclic heterocyclic radical, in which the substituents of A are chosen from the group consisting of C₁-C₈alkyl, C₁-C₈alkoxy, halogen, halo-C₁-C₈alkyl, cyclopropyl, halocyclopropyl, C₂-C₈alkenyl, C₂-C₈alkynyl, halo-C₂-C₈alkenyl, halo-C₂-C₈alkynyl, halo-C₁-C₈alkoxy, C₁-C₈alkylthio, halo-C₁-C₈alkylthio, allyloxy, propargyloxy, allylthio, propargylthio, haloallyloxy, haloallylthio, cyano and nitro;

R is hydrogen, C₁-C₈alkyl, phenyl-C₁-C₄alkyl, C₂-C₈cycloalkyl, C₂-C₈alkenyl or C₂-C₈alkynyl; and

X is N-NO₂ or N-CN,

in the free form or in salt form, if appropriate tautomers, in the free form or salt form, and one or more of the compounds:

(I) aldicarb;	(XIV) zeta-Cypermethrin;	(XXVII) methamidophos;
(II) azinphos-methyl;	(XV) deltamethrin;	(XXVIII) methomyl;
(III) benfuracarb;	(XVI) diflubenzuron;	(XXIX) mevinphos;
(IV) bifenthrin;	(XVII) endosulfan;	(XXX) parathion;
(V) buprofezin;	(XVIII) ethiofencarb;	(XXXI) parathion-methyl;
(VI) carbofuran;	(XIX) fenitrothion;	(XXXII) phosalone;
(VII) dibutylaminothio;	(XX) fenobucarb;	(XXXIII) pirimicarb;
(VIII) cartap;	(XXI) fenvalerate;	(XXXIV) propoxur;
(IX) chlorofluazuron;	(XXII) formothion;	(XXXV) teflubenzuron;
(X) chloropyrifos;	(XXIII) methiocarb;	(XXXVI) terbufos;
(XI) cyfluthrin;	(XXIV) heptenophos;	(XXXVII) triazamate;
(XII) lambda-cy-halothrin;	(XXV) imidacloprid;	(XXXVIII) abamectin;
(XIII) alpha-cypermethrin;	(XXVI) isoprocarb;	(XXXIX) fenobucarb;

- (XL) tebufenozide;
 (XLI) fipronil;
 (XLII) beta-cyfluthrin;
 (XLIII) sflafluofen;
 (L) avermectin B₁ (abamectin);
 (LII) a plant extract which is active against insects;
 (LIII) a preparation which comprises nematodes which are active against insects;
 (LIV) a preparation obtainable from *Bacillus subtilis*;
 (LV) a preparation which comprises fungi which are active against insects;
 (LVI) a preparation which comprises viruses which are active against insects;
 (LVII) AC 303 630;
 (LVIII) acephate;
 (LIX) acrinathrin;
 (LX) alanycarb;
 (LXI) alphamethrin;
 (LXII) amitraz;
 (LXIII) AZ 60541;
 (LXIV) azinphos A;
 (LXV) azinphos M;
 (LXVI) azocyclotin;
 (LXVII) bendiocarb;
 (LXVIII) bensultap;
 (LXIX) betacyfluthrin;
 (LXX) BPMC;
 (LXXI) brofenprox;
 (LXXII) bromophos A;
 (LXXIII) bufencarb;
 (LXXIV) butocarboxin;
 (LXXV) butylpyridaben;
 (LXXVI) cadusafos;
 (LXXVII) carbaryl;
 (LXXVIII) carboxophenothion;
 (LXXIX) chloethocarb;
 (LXXX) chloroethoxyfos;
 (LXXXI) chloromephos;
 (LXXXII) cis-res-methrin;
 (LXXXIII) clopythrin;
 (LXXXIV) clofentezin;
 (LXXXV) cyanophos;
 (LXXXVI) cycloprothrin;
 (LXXXVII) cyhexatin;
 (LXXXVIII) demeton M;
 (LXXXIX) demeton S;
 (XC) demeton-S-methyl;
 (XCI) dichlofenthion;
 (XCII) diclphos;
 (XCIII) diethion;
 (XCIV) dimethoate;
 (XCV) dimethylvinphos;
 (XCVI) dioxathion;
 (XCVII) edifenphos;
 (XCVIII) emamectin;
 (XCIX) esfenvalerate;
 (C) ethion;
 (CI) ethofenprox;
 (XLVIII) pyrimidifen;
 (XLIX) nitenpyram;
 (L) NI-25, acetamiprid;
 (CII) ethoprophos;
 (CIII) etrimphos;
 (CIV) fenamiphos;
 (CV) fenbutatin oxide;
 (CVI) fenothiocarb;
 (CVII) fenpropathrin;
 (CVIII) fenpyrad;
 (CIX) fenthion;
 (CX) fluazinam;
 (CXI) flucycloxuron;
 (CXII) flucythrinate;
 (CXIII) flufenoxuron;
 (CXIV) flufenprox;
 (CXV) fonophos;
 (CXVI) fosthiazate;
 (CXVII) fufenprox;
 (CXVIII) HCH;
 (CXIX) hexaflumuron;
 (CXX) hexythiazox;
 (CXXI) iprobenfos;
 (CXXII) isofenphos;
 (CXXIII) Isoxathion;
 (CXXIV) ivermectin;

(CXXV) lambda-cyhalothrin;	(CXLV) pirimiphos A;	(CLXVI) thiodicarb;
(CXXVI) malathion;	(CXLVI) promecarb;	(CLXVII) thiofanox;
(CXXVII) mecarbam;	(CXLVII) propaphos;	(CLXVIII) thionazin;
(CXXVIII) mesulfenphos;	(CXLVIII) prothiofos;	(CLXIX) thuringlensin;
(CXXIX) metaldehyde;	(CXLIX) prothoate;	(CLXX) tralomethrin;
(CXXX) metolcarb;	(CL) pyrachlophos;	(CLXXI) triarthen;
(CXXXI) milbemectin;	(CLJ) pyrada-phenthion;	(CLXXII) triazophos;
(CXXXII) moxidectin;	(CLJ) pyresmethrin;	(CLXXIII) triazuron;
(CXXXIII) naled;	(CLJII) pyrethrum;	(CLXXIV) trichlorofon;
(CXXXIV) NC 184;	(CLIV) RH 5992;	(CLXXV) triflumuron;
(CXXXV) omethoate;	(CLV) salithion;	(CLXXVI) trimethacarb;
(CXXXVI) oxamyl;	(CLVI) sebufos;	(CLXXVII) vamidothion;
(CXXXVII) oxydemeton M;	(CLVII) sulfotep;	(CLXXVIII) xythylcarb;
(CXXXVIII) oxydeprofos;	(CLVIII) sulprofos;	(CLXXIX) Y1 5301/5302;
(CXXXIX) permethrin;	(CLIX) tebufenpyrad;	(CLXXX) zetamethrin;
(CXL) phenthoate;	(CLX) tebupirimphos;	(CLXXXI) DPX-MP062;
(CXL) phorate;	(CLXI) tefluthrin;	(CLXXXII) RH-2485;
(CXLII) phosmet;	(CLXII) temephos;	(CLXXXIII) D 2341; or
(CXLIII) phoxim;	(CLXIII) terbam;	(CLXXXIV) XMC (3,5-xythylmethylcarbamate),
(CXLIV) pirimiphos M;	(CLXIV) tetrachlorovinphos;	
and at least one auxiliary.	(CLXV) thiafenox;	

2. A composition according to claim 1, in which, in the compound of the formula (A), R is hydrogen, C₁-C₄alkyl, C₃-C₆cycloalkyl, C₂-C₆alkenyl or C₂-C₆alkynyl.

3. A composition according to claim 1 or 2, in which, in the compound of the formula (A), the cyclic base skeleton of A contains 2 to 4 double bonds.

4. A composition according to any one of claims 1 to 3, in which, in the compound of the formula (A), the cyclic base skeleton of A contains 1 up to and including 4 heteroatoms.

5. A composition according to any one of claims 1 to 4, in which, in the compound of the formula (A), the cyclic base skeleton of A contains 1, 2 or 3 heteroatoms, chosen from the group consisting of oxygen, sulfur and nitrogen, not more than one of the heteroatoms contained in the cyclic base skeleton being an oxygen or a sulfur atom.
6. A composition according to any one of claims 1 to 5, in which, in the compound of the formula (A) the cyclic base skeleton of A is mono- or disubstituted by substituents chosen from the group consisting of halogen and C₁-C₃alkyl.
7. A composition according to any one of claims 1 to 6, in which, in the compound of the formula (A), the cyclic base skeleton of A is a pyridyl, 1-oxidopyridinio or thiazolyl group.
8. A composition according to any one of claims 1 to 7, in which, in the compound of the formula (A), X is N-NO₂.
9. A composition according to claim 1, which comprises either
- (A.1) (2-chloropyrid-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine;
 - (A.2) (2-chlorothiazol-5-ylmethyl)-3-ethyl-4-nitroimino-perhydro-1,3,5-oxadiazine;
 - (A.3) 3-methyl-4-nitroimino-5-(1-oxido-3-pyridinylomethyl)-perhydro-1,3,5-oxadiazine;
 - (A.4) (2-chloro-1-oxido-5-pyridinylomethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine;
 - (A.5) (2-chlorothiazol-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine;
 - (A.6) 3-methyl-5-(2-methylpyrid-5-ylmethyl)-4-nitroimino-perhydro-1,3,5-oxadiazine;
 - (A.7) (2-chloropyrid-5-ylmethyl)-4-nitroimino-perhydro-1,3,5-oxadiazine;
 - (A.8) (2-chlorothiazol-5-ylmethyl)-4-nitroimino-perhydro-1,3,5-oxadiazine; or
 - (A.9) (2-chloropyrid-5-ylmethyl)-3-ethyl-4-nitroimino-perhydro-1,3,5-oxadiazine.
10. A composition according to any one of claims 1 to 9, which comprises 5-(2-chlorothiazol-5-ylmethyl)-3-methyl-4-nitroimino-perhydro-1,3,5-oxadiazine.
11. A composition according to any one of claims 1 to 10, which comprises only one of the compounds (I) to (CLXXXIV).
12. A composition according to any one of claims 1 to 11 which comprises pyriproxyfen.
13. A composition according to any one of claims 1 to 11, which comprises fipronil.

14. A composition according to any one of claims 1 to 11, which comprises endosulfan.
15. A composition according to any one of claims 1 to 11, which comprises buprofezin.
16. A composition according to any one of claims 1 to 11, which comprises pirimicarb.
17. A method of controlling pests, which comprises applying a composition as defined in any one of claims 1 to 16, to the pests or their environment.
18. A method according to claim 17, for the protection of plant propagation material, which comprises treating the plant propagation material or the site where the propagation material is brought out.
19. A process for the preparation of a composition comprising at least one auxiliary as defined in any one of claims 1 to 16, which comprises intimately mixing the active compounds with the auxiliary or auxiliaries.
20. Plant propagation material treated by the method defined in claim 18.
21. The use of a composition as defined in any one of claims 1 to 16, in a method as defined in claim 17 or 18.
22. The use of a compound of the formula (A), in the free form or in an agrochemically usable salt form, for the preparation of a composition as defined in any one of claims 1 to 16.

INTERNATIONAL SEARCH REPORT

Enter national Application No.
PCT/EP 97/01926

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N51/00 A01N47/40 //(A01N51/00,43:88,43:56,43:40,43:30)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 580 553 A (CIBA-GEIGY AG) 26 January 1994 cited in the application see the whole document see in particular page 15, lines 17-21; page 17, table 1, compounds 1.2, 1.10, 1.4, 1.5, 1.3, 1.8 and 1.9 and claim 15 --- -/-	1-22

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

26 August 1997

Date of mailing of the international search report

23.09.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentkan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Muellners, W

INTERNATIONAL SEARCH REPORT

 Internat. Application No.
 PCT/EP 97/01926

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CLIVE TOMLIN (ED.): "The Pesticide Manual, 10th. Edition" 1995, BRITISH CROP PROTECTION COUNCIL, FARNHAM, GB; XP002038908 see page 1335 - page 1341 see entry nos.: 17 and 466 see entry nos.: 42, 136, 296, 358, 378, 462, 482, 531, 532, 550 and 662	1-11, 17-22
Y	see entry nos.: 55, 103, 104, 274, 297, 465, 414, 563 and 590	16
Y	see entry nos.: 66, 172, 175, 179, 181, 196, 310 and 173 see entry no. 87	15
Y	see entry no. 106 see entry nos.: 120, 224 and 658 see entry no. 262	14
Y	see entry no. 402 see entry no. 694 see entry no. 1 see entry no. 652 see entry no. 314	13
Y	see entry no. 626 see entry no. 306 see entry no. 603 see entry no. 290 see entry no. 609	12
Y	see entry no. 608 see entry no. 507 see entry no. 502 see entry no. 38 see entry no. 621 see entry nos.: 379, 635 and 636 see entry no. 44 see entry nos.: 49, 50 and 717 see entry nos.: 17 and 433 --- CHEMICAL PATENTS INDEX, DOCUMENTATION ABSTRACTS JOURNAL Week 9542 1 December 1995 Derwent Publications Ltd., London, GB; AN 95-325540 XP002038403 & JP 07 224 062 A (NIPPON BAYER AGROCHEM. K.K.), 22 August 1995 see abstract	1-22
Y	--- EP 0 627 165 A (MILES INC.) 7 December 1994 see page 2, line 20 - line 26; claims 13-18 --- -/--	1-11, 17-22

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/EP 97/01926

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL PATENTS INDEX, DOCUMENTATION ABSTRACTS JOURNAL Week 9507 31 March 1995 Derwent Publications Ltd., London, GB; AN 95-048729 XP002038909 & JP 06 329 508 A (NIPPON BAYER AGROCHEM K.K.) see abstract ---	15
Y	CHEMICAL PATENTS INDEX, BASIC ABSTRACTS JOURNAL Week 8827 31 August 1988 Derwent Publications Ltd., London, GB; AN 88-188016 XP002038852 & JP 63 126 806 A (NIHON TOKUSHU NOYAKU SEI) see abstract ---	16
P,Y	DE 44 43 888 A (BAYER AG) 13 June 1996 see page 7, line 46 - page 13, line 51; example 11 see page 2, line 1 - line 32 ---	12
P,Y	DE 195 19 007 A (BAYER AG) 28 November 1996 see page 2; claims ---	12-14
P,X	WO 96 23411 A (RHONE-POULENC AGROCHIMIE) 8 August 1996 see claims ---	1-11,13, 17-22
A	CHEMICAL PATENTS INDEX, DOCUMENTATION ABSTRACTS JOURNAL Week 9115 12 June 1991 Derwent Publications Ltd., London, GB; AN 91-104761 XP002038910 & JP 03 041 005 A (TAKEDA CHEMICAL IND. K.K.) see abstract ---	1-22
A	CHEMICAL PATENTS INDEX, BASIC ABSTRACTS JOURNAL Week 8827 31 August 1988 Derwent Publications Ltd., London, GB; AN 88-188014 XP002038911 & JP 63 126 804 A (NIHON TOKUSHU NOYAKU SEI) see abstract ---	1-22

	-/--	

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/EP 97/01926

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 431 361 A (NIHON TOKUSHU) 12 June 1991 see page 2, line 3 - line 10; claims 1,3 ---	1-22
A	FR 2 720 230 A (CIBA-GEIGY AG.) 1 December 1995 see page 10, line 29 - page 11, line 12; claims 1,3; examples B1-B5 ---	1-22
A	WO 95 33380 A (CIBA-GEIGY AG) 14 December 1995 see page 1, paragraph 1 - paragraph 2 see page 8, paragraph 2 - paragraph 4; claim 1 -----	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 97/01926

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 580553 A	26-01-94	AU 4210793 A	27-01-94
		BG 97962 A	25-04-94
		BR 9302943 A	16-02-94
		CA 2100924 A	23-01-94
		CN 1084171 A	23-03-94
		CZ 9301457 A	16-02-94
		HR 931073 A	30-04-96
		HU 65131 A	28-04-94
		JP 6183918 A	05-07-94
		NZ 248195 A	27-02-96
		PL 299755 A	05-04-94
		SK 76493 A	08-06-94
		ZA 9305263 A	09-02-94
EP 627165 A	07-12-94	AU 6191594 A	08-12-94
		BR 9402153 A	27-12-94
		JP 6340515 A	13-12-94
		ZA 9403811 A	31-01-95
DE 4443888 A	13-06-96	AU 4256996 A	26-06-96
		WO 9617520 A	13-06-96
		FI 972387 A	05-06-97
		ZA 9510433 A	18-06-96
DE 19519007 A	28-11-96	AU 5818596 A	11-12-96
		WO 9637105 A	28-11-96
WO 9623411 A	08-08-96	FR 2729824 A	02-08-96
		FR 2729825 A	02-08-96
		AU 4626996 A	21-08-96
EP 431361 A	12-06-91	JP 3167106 A	19-07-91
		CN 1052240 A,B	19-06-91
		DE 69006833 D	31-03-94
		DE 69006833 T	01-06-94
		US 5521176 A	28-05-96
		US 5140019 A	18-08-92
		US 5260312 A	09-11-93
FR 2720230 A	01-12-95	CH 688216 A	30-06-97

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 97/01926

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2720230 A		JP 7330517 A	19-12-95
WO 9533380 A	14-12-95	AU 2616695 A	04-01-96
		BR 9502710 A	09-04-96
		EP 0765120 A	02-04-97
		ZA 9504683 A	08-12-95